

Chlor-alkali electrolysis

Time required: 40-50 min

Aims of the experiment

- Carry out a chlor-alkali electrolysis to produce chlorine gas and sodium hydroxide.
- Understand a chemical engineering method.
- Examine a chlor-alkali cell as a secondary element.

Principles

Chlor-alkali electrolysis is used to prepare chlorine gas, hydrogen and sodium hydroxide from a solution of rock salt (sodium chloride). This method is currently the best way to prepare chlorine gas, hydrogen and sodium hydroxide from water and sodium chloride, even at commercial scale.

Chlor-alkali electrolysis can be done according to the *diaphragm method*, the *membrane process* or the *amalgam process*. Although the membrane process is ecological and sustainable, far more than 50% of producers continue to use the amalgam and diaphragm processes.

In the amalgam process, sodium amalgam is prepared in an intermediate reaction using toxic mercury, and this amalgam reacts in a second reaction to form the desired products. Mercury is continuously introduced as a thin film, and is purified and returned in a recirculation loop. In the diaphragm method, asbestos, which is carcinogenic, is used as the diaphragm since it is impermeable to gases.

In the membrane process, a cationic exchange membrane is used which replaces the diaphragm. It is made of sulfonated PTFE (Nafion®). This makes the membrane impermeable for anions and gases. Only cations can pass through. Because of the impermeability to chloride, a sodium hydroxide solution results which is hardly contaminated by rock salt (conc. 30-33 %).

What is happening during the electrolysis?

At the beginning, the anode space is filled with aqueous sodium hydroxide solution. At the graphite anode, the chloride ions are oxidised to form chlorine gas. At the cathode, elemental hydrogen is formed through reduction. Finally, hydroxide ions and sodium cations remain in the solution, and as the solution is concentrated further, this produces solid sodium hydroxide. However, some hydroxide ions migrate to the anode space because of the electric field and there they enter into an undesired secondary reaction with free chloride ions to form hypochlorite.

The possible electrode reactions are listed below.

		Redox-potential
An-ode	$2 \text{Cl}^- \rightarrow 2 \text{Cl}_2 + 2 \text{e}^-$	1.35 V
	$2 \text{Cl}^- \rightarrow 2 \text{Cl}_2 + 2 \text{e}^-$	1.24 V
	(6M NaCl)	
	$\rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^-$	0.81 V
	$2 \text{OH}^- (\text{pH} = 7) \rightarrow \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^-$	1.23 V
Cath-ode	$3 \text{H}_2\text{O} (\text{pH} = 0) \rightarrow 2 \text{H}_2\text{O} + \text{H}_2$	0 V
	$2 \text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2 \text{H}_2\text{O} + \text{H}_2$	(pH = 0)
	$2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2$	-0.83 V
	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}^0$	(pH = 14) -2.7 V

If we take a close look at the reactions, chlorine gas generation should not be thermodynamically possible since according to the potential, water is electrolysed beforehand. However, as in all chemical reactions, electrochemically-induced reactions also need a certain activation energy, and thus proceed from a kinetic point of view as well. The activation energy can be derived from what is called "overvoltage". The overvoltage is the voltage which must be applied in order to drive the electrochemical reaction. However, the overvoltage depends strongly on the electrode material. The overvoltage



Fig. 1: Set-up and materials for the experiment.

of water on carbon is greater than that for chloride oxidation. Therefore, water will not oxidise, but chlorine will.

In this experiment, chlorine and sodium hydroxide formation will be carried out and qualitatively monitored using an aqueous rock salt solution with an indicator solution.

Risk assessment

CAUTION! Small amounts of toxic chlorine gas will arise during electrolysis. Carry out the experiment in the fume hood or make sure there is good ventilation.

Universal indicator solution	
  Signal word: Hazard	<p>Hazard warnings</p> <p>H225 Highly flammable liquid and vapour.</p> <p>H319 Causes serious eye irritation.</p> <p>Safety information</p> <p>P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.</p> <p>P280 Wear protective gloves / eye protection.</p> <p>P305+P351+P338 IN CASE OF CONTACT WITH EYES: carefully flush with water for several minutes. Remove contact lenses if present and if possible to do so. Continue to rinse.</p> <p>P337+P313 If eye irritation persists: Get medical advice/attention.</p>
Sodium hydroxide solution	
 Signal word: Caution	<p>Hazard warnings</p> <p>H314 Causes severe skin burns and severe eye damage.</p> <p>H290 May be corrosive to metals.</p> <p>Safety information</p> <p>P280 Wear protective gloves / eye protection.</p> <p>P301 + P330 + P331 if swallowed: Rinse mouth. Do not induce vomiting.</p> <p>P305+P351+P338 IN CASE OF CONTACT WITH EYES: carefully flush with water for several minutes. Remove contact lenses if present and if possible to do so. Continue to rinse.</p> <p>P309+P310 If exposed or you feel ill: Immediately call the POISON CENTRE and/or consult a physician.</p>

Chlorine gas	
    Signal word: Hazard	<p>Hazard warnings</p> <p>H270 May cause or intensify fire; oxidizer</p> <p>H280 Contains gas under pressure; may explode if heated.</p> <p>H315 Causes skin irritation.</p> <p>H319 Causes serious eye irritation.</p> <p>H330 Hazardous to health if inhaled.</p> <p>H335 May cause respiratory irritation.</p> <p>H400 Very poisonous to aquatic organisms.</p> <p>Safety information</p> <p>P260 Do not breathe dust/fume/gas/mist/vapours/spray.</p> <p>P220 Keep/store away from clothing/combustible materials.</p> <p>P280 Wear protective gloves / eye protection.</p> <p>P244 Keep pressure regulator away from grease and oil.</p> <p>P273 Avoid release into the environment.</p> <p>P304+P340 If inhaled: Bring person to fresh air and make sure airways are not blocked.</p> <p>P305+P351+P338 IN CASE OF CONTACT WITH EYES: carefully flush with water for several minutes. Remove contact lenses if present and if possible to do so. Continue to rinse.</p> <p>P332+P313 In case of skin irritation: Get medical advice/attention.</p> <p>P370+P376 In case of fire: Fix leaks if it can be done safely.</p> <p>P302+P352 If on skin: Wash with lots of soap and water.</p> <p>P315 Get medical advice/attention.</p> <p>P405 Store locked up.</p> <p>P403 Store in a well ventilated place.</p>

Equipment and chemicals

1	Electrochemistry demonstration unit, CPS	664 4071
1	Panel frame C50, two-level, for CPS	666 425
1	Electrochemistry table, CPS	666 472
1	Electrochemistry accessories set.....	664 401
1	Electrolysis cell	from 664 401
2	Paper diaphragm.	from 664 401
1	Drip pan	from 664 401
3	Connecting leads	from 664 401
2	Crocodile clips	from 664 401
2	Carbon electrodes	from 664 401
1	Measuring scales.....	ADABC501
1	Beaker, 250 ml.....	664 130
1	Measuring cylinder, 100 ml.....	665 754
1	Sodium chloride, 500 g.....	673 5710
1	Universal indicator solution, 50 ml.....	675 2550

Set-up and preparation of the experiment

Set-up of the experiment

Suspend the demonstration unit (Fig. 2) and the electrochemistry table in the panel frame. Place the drip pan in the centre of the electrochemistry table. Fix the two half cells of the electrolysis cell with the screws so that a gap about 0.5 cm wide remains open. Now, place two overlapping paper diaphragms into them and tighten the screws. The electrolysis cell should now be sealed.

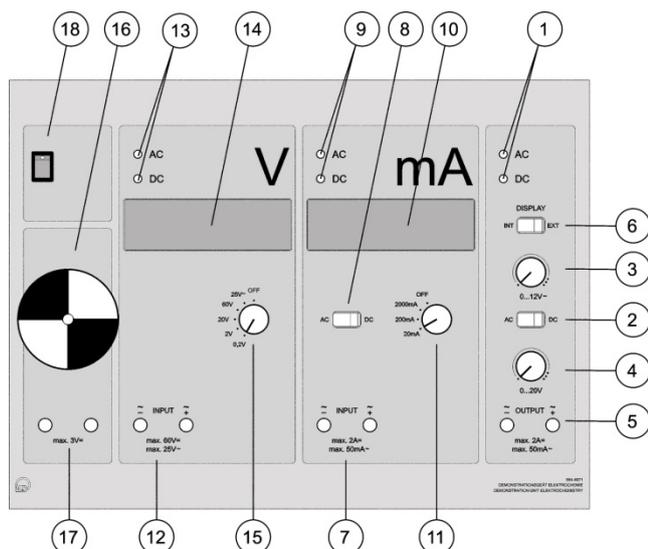


Fig. 2: Sketch of the demonstration unit.

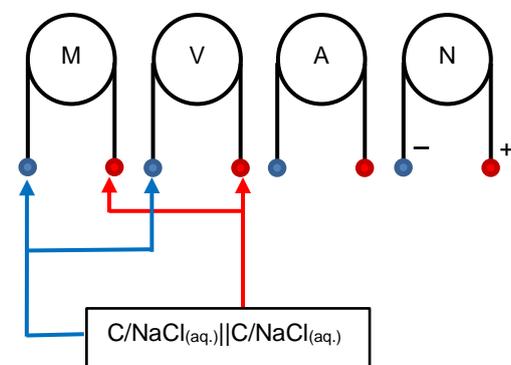


Fig. 2: Circuit for the experiment during discharging.

Preparation of the experiment

Place 9 g of sodium chloride in a beaker (250 ml). Now add 150 ml of distilled water (measuring cylinder) to the beaker in

order to obtain an approximately 1 molar NaCl solution. Place a carbon electrode into each second outermost groove. Connect the outlet jacks of the power supply (5) to the carbon electrodes using the connecting leads.

Set the changeover switch (2) to direct current (DC) at the power supply (5). Also set the changeover switch (8) and rotary controller (15) to direct current (DC). Place the measurement display at selector switch (6) to internal power source (see Fig. 2).

Performing the experiment

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Distribute the NaCl solution evenly between both half cells. In the process, raise the carbon electrodes slightly so that the level in the overall electrolysis cell is the same.

In the cathode space and anode space, place a few drops of the indicator solution and homogenise by lightly shaking.

Turn on the demonstration unit using switch (18). Set a direct current of 3V using controller (4) and electrolyse for 10 minutes. Then, end the reaction by turning off the demonstration unit.

Note the changes in the electrodes. What happened? Is there any discernible odour?

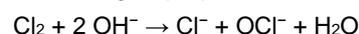
Observation

Chlor-alkali electrolysis

Visible gas generation is taking place at both electrodes. An odour can be discerned that is similar to that at swimming pools. In the cathode space there is a noticeable colour change happening, initially at the cathode and later throughout the entire space. Likewise in the anode space. The colour is decreasing over time in the anode space.

Evaluation

During electrolysis, a chlorine odour is discernible. In addition, discolourations in the indicator solution can be seen. The reason for this is that initially, in the cathode space, sodium hydroxide is being produced at the cathode. This discolours the solution blue. In the anode space, in addition to the generation of chlorine, hypochlorous acid is also being generated according to the following disproportionation reaction.



However, the colour fades after some time since the hypochlorite has known bleaching properties, which oxidises the dye molecules in the indicator solution.

Results

Chlor-alkali electrolysis for preparing chlorine gas and sodium hydroxide is a very well established commercial scale process. Even scaling it down to laboratory scale does not cause problems. The odour clearly indicates the formation of chlorine gas. By adding an indicator solution, the formation of sodium hydroxide can be monitored. Likewise, the formation of the secondary product, hyperchloric acid, can be monitored.

Further procedure

The chlor-alkali cell as a secondary element

Chlor-alkali cells can also be retrofitted as secondary elements. To do so, switch the selector switch (6) to external power supply. Connect the positive outlet jack (12) to the cathode. Connect the anode to an output (17) of the electric

motor. Connect the other output of the electric motor to the negative output jack (12). By turning on the demonstration unit (18), the clamping voltage can be read off at the display (14). Also, by connecting the electric motor, the load current and discharging can be followed. Here, the voltage should be read off and recorded every minute. After 20 minutes, the experiment can be ended by turning off the demonstration unit.

The electrolysis was carried out for 10 minutes at a voltage of 3V. The drop in voltage during discharging was followed for 20 minutes. The following table contains the voltage values.

Tab. 1: Voltage values with a load at the cell

Time [min]	Voltage [V]
0	2.35
1	1.65
2	1.03
3	0.72
4	0.64
5	0.48
6	0.45
7	0.41
8	0.32
9	0.27
10	0.22
11	0.18
12	0.15
13	0.13
14	0.12
15	0.11
16	0.10
17	0.097
18	0.095
19	0.093
20	0.091

All values can now be graphically represented. Here, the voltage is plotted against time in order to obtain a voltage curve.

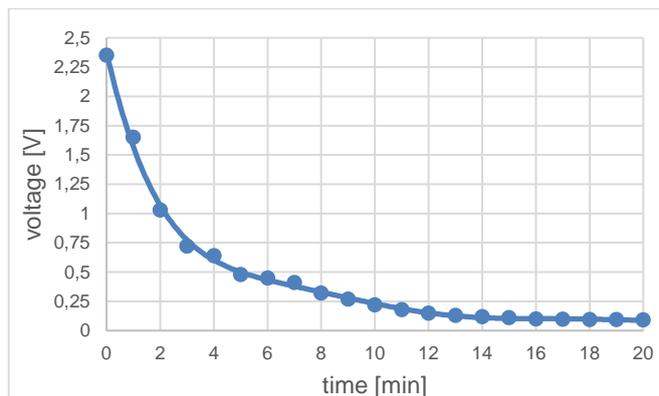


Fig. 3: Voltage curve with a load at the cell. Clamping voltage is 2.35 V. The voltage decreases significantly until a constant value is reached.

A chlor-alkali cell such as this is not well suited as a secondary element. The clamping voltage does provide very good values of 2.35V, but commercial use is not possible since the voltage decreases quickly under load. Even if this were not the case, toxic chlorine gas would be released during charging of the cell, which would make everyday use impossible.

Cleaning and disposal

All solutions can be disposed of in the laboratory drain with plenty of water.